High resolution lifetime measurements of the perturbed J'=0 levels of the 1B3u state of pyrazine

van Herpen, Willy M.; Meerts, W. Leo; Drabe, Karel E.; Kommandeur, Jan

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.452732

Publication date:
1987

High resolution lifetime measurements of the perturbed J'=0 levels of the $^1B_{3u}$ state of pyrazine

Willy M. van Herpen, W. Leo Meerts, Karel E. Drabe, and Jan Kommandeur

Citation: The Journal of Chemical Physics **86**, 4396 (1987); doi: 10.1063/1.452732
View online: https://doi.org/10.1063/1.452732
View Table of Contents: http://aip.scitation.org/toc/jcp/86/8
Published by the American Institute of Physics

High resolution lifetime measurements of the perturbed $J'=0$ levels of the $^1B_{3u}$ state of pyrazine

Willy M. van Herpen and W. Leo Meerts
Fysisch laboratorium, Katholieke Universiteit, Toernooiveld, 6525 ED Nijmegen, The Netherlands
Karel E. Drabe[a] and Jan Kommandeur
Laboratory for Physical Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

(Received 17 July 1986; accepted 8 January 1987)

The lowest excited singlet $^1B_{3u}$ state of pyrazine is known to be coupled to a number of triplet $^3B_{3u}$ states. Using a strongly collimated molecular beam and a single frequency laser it is shown that the $J'=0$ of the 0_0^0 transition contains at least 36 states. We have individually excited eight of these states and studied its decay. The lifetimes found (typically 450 ns) do not scale with the intensities of the excitation spectrum. This deviation is caused by a nonradiative decay of the zero order $^3B_{3u}$ states. With a simple model it was possible to reconstruct the absorption spectrum, the energies of the zero order states and its coupling strengths. The zero order decay rates of the singlet and triplet states have been determined. The value obtained for the zero order singlet state is 5 MHz; the values for the triplet states range from 0.6 to about 5 MHz.

I. INTRODUCTION

Van der Meer *et al.*[1] have recently shown that the $^1B_{3u} \leftarrow {}^1A_g 0_0^0$ band of pyrazine contains many more lines than expected for an ordinary allowed electronic transition. This additional structure originates from a coupling between the electronic S_1 state and isoenergetic levels of the lowest triplet (T) state. It was found that the $S_1 \leftarrow S_0$ transition has the characteristics of a c-type spectrum of a near oblate symmetric top. Transitions corresponding to different values of the total quantum number J were well separated. Different $J' \leftarrow J''$ transitions in the P and R branch of the band could therefore easily be assigned. However, the K-rotational structure turned out to be of the same order of magnitude as the splittings due to the S_1–T coupling. Consequently no complete rotational assignment was possible with the exception of $P(1)$ and $R(0)$ transition. These transitions only connect states with $K_c = 0$. In the absence of S_1–T interactions these transitions should appear as a single line. In studying the $P(1)$ transition we solely probe the $J'=0$, $K_c=0$ state of the S_1 excited level. It is therefore that we have investigated the $P(1)$ transition in more detail in this work. The spectrum first observed in Ref. 1 has presently been recorded with a larger dynamical range and is shown in Fig. 1. The original spectrum from Ref. 1 was interpreted in terms of a coupling between the S_1 and a number of triplet states. From the spectrum Van der Meer *et al.*[2] determined the relative energies of and the couplings strengths between the zero order states. The procedure used a dediagonalization of the energy matrix to a bases of the zero order states. In order to be successful, relative energy positions and steady state absorption intensities of the lines in the $P(1)$ transition are needed. Unfortunately experimentally we observe a laser *excitation* spectrum. The relation between the two different spectra and the validity of the dediagonalization method will be discussed.

Recently Amirav *et al.*[3] studied the absolute fluorescence quantum yield from photoselected rotational states. Their interpretation of the rotational dependence of the quantum yield is based on the radiative and nonradiative decay width of each molecular eigenstate (ME). De Lange *et al.*[4] also investigated the rotational dependence of the quantum yield. They showed that the radiationless decay of the $^1B_{3u}$ electronic state for $J' \leqslant 4$ is due to Corriolis coupling. If this were the only radiationless process, the excitation spectrum should be proportional to the absorption spectrum. The magnitude of a possible nonradiative width of the zero order triplet states will determine whether the assumption of proportionality between the excitation spectrum and the absorption spectrum is correct. Since this assumption plays an important role in the understanding of the radiationless decay of the S_1 state of pyrazine[1–6] an attempt was undertaken in this paper to derive the absorption spectrum of the $J'=0$ states. We therefore studied the lifetimes of individual molecular eigenstates in the $P(1)$ transition. This allowed us to extract the absorption spectrum from the excitation spectrum and to determine the decay rates of the zero order states.

II. EXPERIMENTAL

In order to resolve the molecular eigenstates of the 0_0^0 transition of pyrazine we have used a molecular beam setup in combination with a single frequency dye laser. The apparatus situated at Nijmegen, was described in detail before[7,8] and only a brief description of the most relevant features is given here. Pyrazine was seeded with argon and expanded by a continuous nozzle (100 μm diameter) at a backing pressure of 0.5 atm in a vacuum chamber. The source was kept at room temperature and the rotational temperature obtained is estimated to be about 3 K. The molecular beam was strongly collimated by two conical skimmers. In the interac-

[a] Present address: Physical Chemical Laboratory, Vrije Universiteit, de Boelenlaan 1083, 1081 HV Amsterdam, The Netherlands.

 0021-9606/87/084396-05$02.10

tion zone with the radiation field, 30 cm from the beam orifice, the residual Doppler width was 15 MHz. The undispersed laser induced fluorescence was imaged to the photocathode of a photomultiplier tube (EMI 9863/350 QA).

The narrow band radiation field was obtained by second harmonic generation[9] in a modified ring dye laser (Spectra Physics). For this purpose a $LiIO_3$ angle tuned crystal was placed inside the laser cavity. About 2 mW of cw UV power was produced with a bandwidth of less than 0.5 MHz. Relative frequencies have been measured by a sealed off temperature stabilized Fabry–Perot interferometer.

For recording the $P(1)$ spectrum of Fig. 1 the spectrometer was computer controlled by a PDP11/23plus. The laser induced fluorescence collected was detected by a standard photon counting system interfaced with the microcomputer. The molecular beam was chopped and phase sensitive detection was applied to suppress background radiation.

For the lifetime measurements the laser was held on the peak of a transition to a ME while the laser radiation was modulated with an electro-optic modulator (Coherent Radiation) in conjunction with a polarizer. This resulted in single frequency pulses of 40 ns duration with a light on and off ratio of about 150. The repetition rate was 12 kHz. The photons emitted upon excitation of pyrazine were detected using a single photon counting technique. Pile up was prohibited by a pile-up inhibitor. For the two strongest lines in the spectrum about 0.1 photon per shot was detected.

III. RESULTS FOR $P(1)$

Since the first data on pyrazine were taken[1] considerable improvements on the spectrometer allowed us to obtain more detailed spectra of the $^1S_1 \leftarrow {}^1S_0$ transition in this molecule. Figure 1 shows the present results. The improvements were found in a stronger and better cooled molecular beam, reduction of the residual Doppler width to 15 MHz and optimization of the optical system. Furthermore the dynamic detection range was increased with the help of digital data recording. The spectrum of Fig. 1 is taken with a preset counting time of the photon counter of 0.1 s and has a signal-to-noise ratio of 10^3. This spectrum shows many more details of weak well resolved transitions. The 12 previously observed features[1] in the $P(1)$ transition are, of course, also reproduced. A total of 36 lines has been counted from the spectrum of Fig. 1. Table I lists the relative frequencies and intensities. The accuracy in the frequency scale is limited by thermal drift of the marking interferometer and is estimated to be about 1.5% while the intensities have an uncertainty of 5%. For eight of the stronger lines in the $P(1)$ spectrum we could study the decay after excitation with a 40 ns pulse. Figure 2 shows the decay of the strongest line of the $P(1)$ spectrum. It was found that all observed decays showed within experimental accuracy single exponential behavior. The lifetimes τ of the excited state levels were determined by a least-square fit of each of the decay curves over a period of at least 4τ. The results are listed in Table I. We estimate an accuracy of about 50 ns in τ. This is mainly due to limitations in the detection system and the background caused by the finite contrast ratio of the optic modulator.

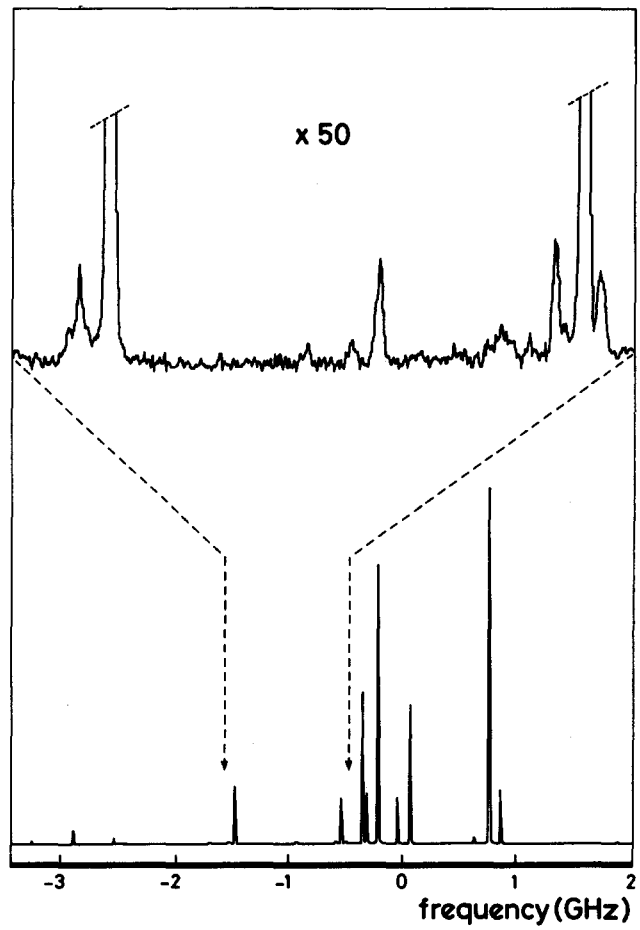

FIG. 1. Excitation spectrum of the $P(1)$ transition of pyrazine at $\nu = -12\,192$ MHz relative to the origin of the $^1B_{3u} \leftarrow {}^1A_g$ electronic transition.

The $^1S_1$ ($^1B_{3u}$) $\leftarrow {}^1S_0$(^1A_g) optical transition in pyrazine dictates a c-type rotational spectrum. Since the molecule is a near symmetric top molecule, the only features in the spectrum are transitions of the type $\Delta K_c = 0$, where K_c represents projection of the rotational quantum number J on the c axis. Therefore, all transitions in the $P(1)$ spectrum arise from one single $|J,K_c\rangle$ ground state. Consequently, the integrated steady state excitation intensities all contain the same Boltzmann population factor. This situation is unique in the $P(1)$ and $R(0)$ transitions in contrast to the other branches, e.g., $P(2)$. Figure 3 shows the rate constants ($\gamma_{ME} = 1/\tau$) vs the excitation intensity for the studied levels in the $P(1)$ perturbed transition. This figure clearly demonstrates that, primarily for the weaker lines, the decay rates are not proportional to the steady state intensities. In Sec. IV we will discuss the consequence of this observation.

IV. THEORY

A molecular eigenstate in the excited electronic state can formally be expanded in the zero order singlet state $|S\rangle$ and a set of triplet states $\{|T\rangle\}$ by

$$\Phi_{MEi} = C_{Si}|S\rangle + \sum_T C_{Ti}|T\rangle. \quad (1)$$

The zero order states have their own independent decay channels with rates γ_S and $\{\gamma_T\}$, respectively. We assume

TABLE I. Energies,[a] excitation intensities, and lifetimes belonging to the $P(1)$ member of the $^1B_{3u}$ 0_0^0 transition of pyrazine. Also the calculated relative absorption intensities are given.

Energy (MHz)	Excitation intensity	Lifetime (ns)	Absorption intensity
− 4725	18		
− 4337	42		
− 3849	20		
− 3686	21		
− 3245	81		
− 2884	376		
− 2530	179		
− 2438	33		
− 2341	22		
− 1881	21		
− 1770	28		
− 1694	39		
− 1536	28		
− 1515	58		
− 1456	1 666	200 (50)	0.118
− 1071	19		
− 984	20		
− 929	58		
− 689	30		
− 637	25		
− 589	66		
− 535	1 278	512	0.065
− 502	55		
− 353	3 891	443	0.122
− 318	1 441		
− 221	8 168	342	0.200
− 44	1 305	437	0.071
62	4 031	560	0.110
593	21		
631	199		
765	10 000	280	0.245
867	1 503	529	0.069
1443	28		
1867	55		
2722	28		
2781	29		

[a] The ME energies are referred to the center of gravity of the excitation spectrum which is at $\nu = -12\,192$ MHz relative to the electronic origin ν_0 of the $^1B_{3u} \leftarrow {}^1A_g 0_0^0$ transition.

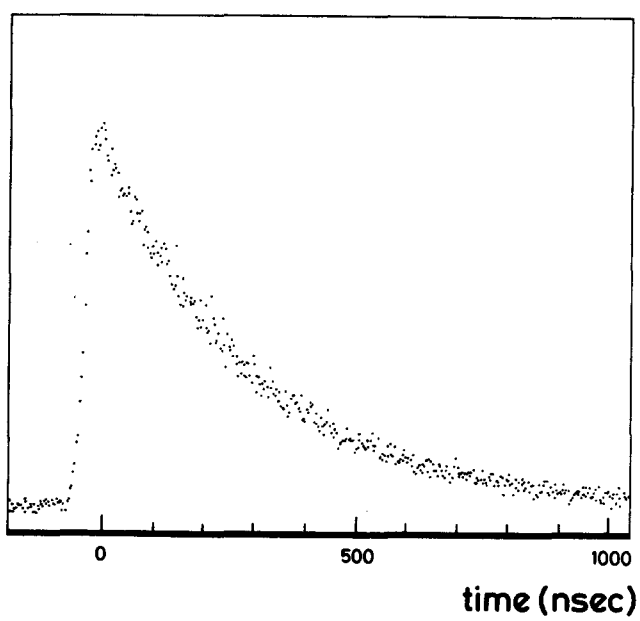

FIG. 2. Decay curve of the strongest line of the $P(1)$ transition.

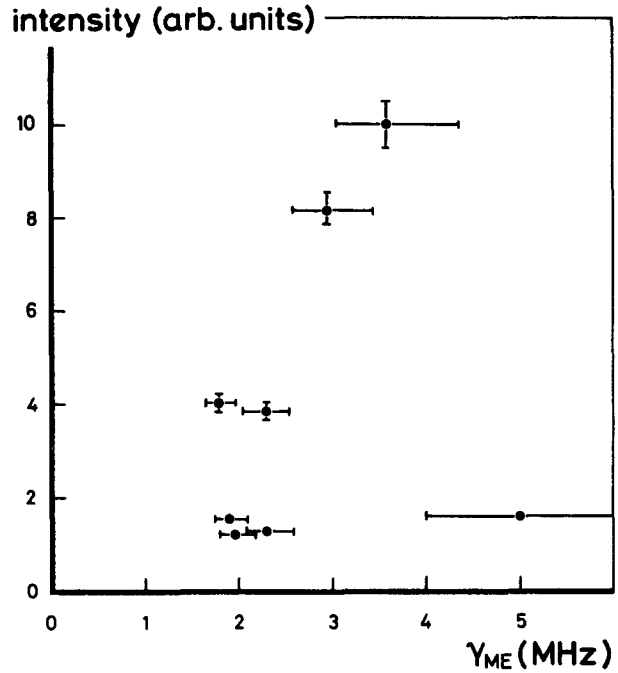

FIG. 3. Relation between the decay rates and the excitation intensity for $P(1)$ lines of pyrazine.

that there is no decay within the triplet states involved in the sum of Eq. (1). In that case the decay rate of the ith molecular eigenstate is given by

$$\gamma_{MEi} = |C_{Si}|^2\gamma_S + \sum_T |C_{Ti}|^2\gamma_T. \tag{2}$$

It is thus supposed that there is no significant decay within the zero order state manifold. The zero order width γ_S can be split in a radiative γ_S^r and nonradiative γ_S^{nr} contribution with

$$\gamma_S = \gamma_S^r + \gamma_S^{nr}. \tag{3}$$

The nature of γ_T may also be radiative or nonradiative. We can safely assume it to be of nonradiative character, since the phosphorescence rate of pyrazine is small.

The steady-state absorption intensity A_i of the ith ME is

$$A_i \propto |\mu_{MEi}|^2 I_l = |\mu_S|^2 |C_{Si}|^2 I_l, \tag{4}$$

where μ_{MEi} and I_l are the ith transition dipole moment of the zero order singlet state and the laser intensity, respectively. A linear laser intensity response is assumed since no saturation effects were observed at a 2 mW laser power level.

Experimentally we observe in the frequency spectrum the steady-state excitation intensity E_i integrated over its inhomogeneous line profile, which is given by

$$E_i \propto \frac{A_i\gamma_{MEi}}{\gamma_{MEi}}$$

$$\propto \frac{\gamma_S^r |\mu_S|^2 I_l |C_{Si}|^4}{\gamma_{MEi}} \tag{5}$$

or

$$E_i = \frac{\alpha |C_{Si}|^4}{\gamma_{MEi}}. \quad (6)$$

Here α is a constant (independent of the ME's) and γ_{MEi} the radiative decay rate of the ith ME. If the decay rates of the molecular eigenstates are dominated by the singlet decay ($\gamma_S \gg \gamma_T$, or $\gamma_T \approx 0$), Eq. (2) can be rewritten as

$$\gamma_{MEi} = |C_{Si}|^2 \gamma_S \quad (7)$$

and the excitation intensity becomes

$$E_i = \frac{\alpha |C_{Si}|^2}{\gamma_S}. \quad (8)$$

In this case the absorption and excitation intensities both scale with the singlet intensity $|C_{Si}|^2$. It also follows that E_i is proportional to its corresponding decay rate γ_{MEi}.

V. RECONSTRUCTION OF THE ZERO ORDER SITUATION

The reconstruction of the zero order states is beset by the problem that one measures excitation spectra rather than absorption spectra. In an earlier publication[2] it was assumed that the excitation spectrum was directly proportional to the absorption spectrum, which implied that the zero order triplet states did not decay on their own. This then implies that the decay rates of the ME's would be proportional to their excitation intensity. Looking at Table I at the intensities of the strongest lines and their decay, it is clear that deviations exist, as is also shown in Fig. 3. The line with the highest relative excitation intensity (10 000) has approximately the same decay rate as the one with an excitation intensity six times lower (1 666)! This clearly demonstrates the existence of a nonzero nonradiative decay (γ_T) of the zero order triplet states. Therefore, the absorption and excitation spectra differ in relative intensities.

In principle we can derive the absorption spectrum from the excitation spectrum and reconstruct the zero order energies, coupling matrix elements and lifetimes of the states $|S\rangle$ and $\{|T\rangle\}$ in three steps:

(i) Experimentally we determine the excitation intensities and lifetimes of the ME's in the $P(1)$ transition. We can then derive the absorption spectrum by utilizing Eq. (6):

$$|C_{Si}|^2 = (E_i \gamma_{MEi}/\alpha)^{1/2}. \quad (9)$$

Here the constant α is determined by experimental conditions such as sensitivity of the detection system. In principle α can be calculated using $\Sigma_i |C_{Si}|^2 = 1$ and Eq. (9) if γ_{MEi} is measured for all ME's. However, in order to find the absorption spectrum only the relative values for $|C_{Si}|^2$ are needed.[2,10]

(ii) The exact and unique dediagonalization procedure of Lawrance and Knight[10] can now be applied to the absorption spectrum obtained in step (i). The method described in Ref. 10 gives an elaborate procedure, involving a Green's function inversion approach, to compute the zero order energies of the states $|S\rangle$ and $\{|T\rangle\}$, together with the coupling elements V_{ST}. In this procedure the steady state absorption intensities and relative energy positions of the lines in the $P(1)$ transition are needed. An essential condition is the fact that only one state component ($|S\rangle$) carries oscillator strength with respect to the initial state. The solution for the zero order states and coupling strengths is unique and its accuracy is limited only by the uncertainties in the experimental data.

(iii) The dediagonalization from step (ii) also provides the composition of the projection of the ME states on the zero order singlet and triplet states (C_{Si}, $\{C_T\}$). Equation (2) yields a set of linear equations with the same number of decay rates (γ_S,$\{\gamma_{Ti}\}$). The solution of these equations thus gives the decay rates of the zero order states.

Unfortunately not all γ_{ME}'s could be measured because of the low excitation intensities of some ME's. Therefore, let us first assume that the widths of the ME's of which the

TABLE II. Relative energies,[a] singlet–triplet coupling matrix elements, and rate constants[b] of the zero order triplet states. The reconstruction of the $P(1)$ absorption spectrum of pyrazine has been performed for the eight strongest lines and for all 36 lines separately. All values are in MHz.

	8 States			36 States		
	Energy	V_{ST}	γ	Energy	V_{ST}	γ
Singlet	−43		5(4)	−362		7.3
Triplet				−4705	270	2.0
				−4307	327	2.0
				−3832	220	2.0
				−3666	250	2.0
				−3216	267	1.9
				−2823	370	1.9
				−2496	236	1.9
				−2414	249	2.0
				−2319	265	2.0
				−1872	110	2.0
				−1761	103	1.9
				−1683	114	1.9
				−1533	39	1.9
				−1509	54	1.8
	−1286	462	5(1)	−1291	479	5.6
				−1062	122	1.9
				−976	99	1.9
				−913	158	1.9
				−684	59	1.9
				−633	49	2.0
				−584	50	1.9
	−502	119	1.6(0.5)	−513	74	1.0
				−486	120	2.6
	−308	105	1.6(0.5)	−334	47	1.4
				−282	102	1.8
	−98	150	2.7(0.5)	−89	160	2.4
	13	117	0.6(0.5)	17	133	0.7
	463	457	3(2)	459	474	3.9
				598	66	1.8
				650	120	1.5
	848	67	1(0.5)	849	76	1.4
				1433	116	2.0
				1849	184	2.0
				2702	245	2.0
				2962	234	2.0

[a] The energies are relative to the center of gravity of the complete excitation spectrum. The position of the singlet level is at the center of gravity of the absorption spectrum and therefore is not necessary at 0 MHz.

[b] The indicated error ranges are introduced by experimental uncertainties in lifetimes and intensities.

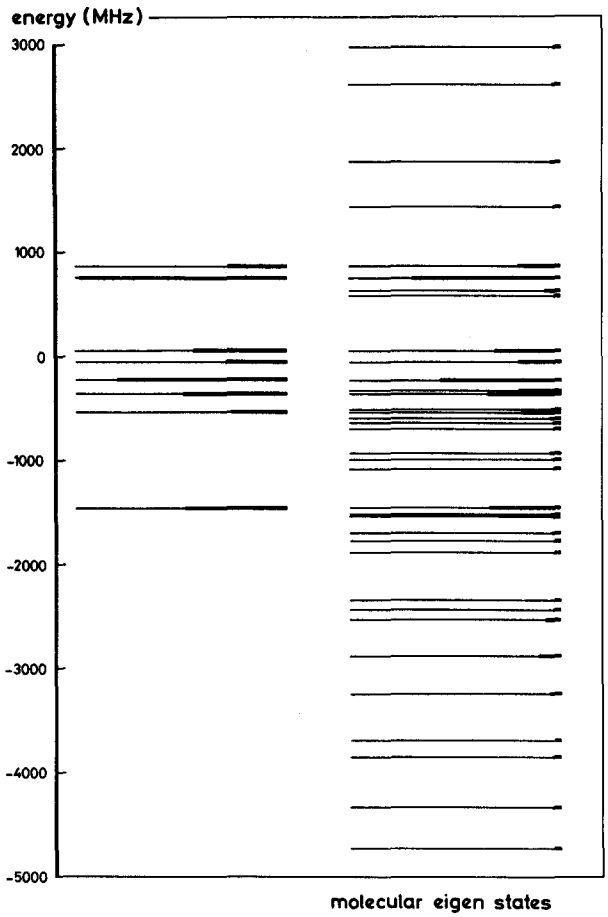

FIG. 4. Composition of the ME's from the analysis of eight states and of all 36 states. The dark part of the line represents the singlet content ($|C_{Si}|^2$). A full line indicates 25% singlet character.

lifetimes were not measured are zero. (This is obviously wrong, since we do measure an excitation intensity at their position). The eight states of which the lifetimes have been determined contain the major part (91%) of the total excitation intensity. Applying the procedure described above, we can then derive the absorption spectrum, which will now consist of only eight lines. The relative absorption intensities are given in Table I, while the zero order energies of the states $|S\rangle$ and $\{|T\rangle\}$, together with their widths and the coupling elements V_{ST} are given in Table II. The uncertainties indicated include the experimental errors in the lifetime and intensity measurements and the correlations between the parameters introduced by the described procedure. The width of the zero order singlet state has a lower limit of 3.3 MHz, which is imparted to it by the pure radiative lifetime of 290 ns, determined independently[11–13] from the absorption intensity. Our solution indeed satisfies this constraint.

Neglecting those ME's for which no lifetime measurements are available, will introduce an extra uncertainty in the final numbers. As we will show this will not substantially affect the conclusion given below. We can investigate the case in which we give all ME's without a measured lifetime an assumed lifetime under the condition that the width of the singlet state exceeds 3.3 MHz. Using the dediagonalization procedure we find that the assumed lifetimes must then exceed 450 ns. It also apears that these lifetimes have an upper limit of about 700 ns in order to give valid solutions for the zero order decay rates. In Table II the calculated results are given for the zero order states, their couplings and their widths in case we assume a lifetime of 500 ns for the unknown values. The energy of the singlet state is shifted considerably, but the triplet states, their widths and the coupling elements are not very much affected.

The purpose of the foregoing was mainly to compare the singlet character of the ME's, i.e., their relative absorption intensities, in case we use the eight strongest lines and in case of the full set of 36 states. Figure 4 displays the result for both calculations. It will be clear that including the full set just leads to a slight redistribution of the singlet amplitudes. This gives an *a posteriori* justification of our procedure.

VI. CONCLUSION

It was unambiguously shown that excitation to a single ME state in the $P(1)$ transition gives rise to a single exponential decay of such a ME. The present study is the first to demonstrate this experimentally in pyrazine. It was further found that the excited S_1 state of pyrazine has nonzero radiationless decay channels for both the zero order singlet and triplet states. The decay rates for the two channels have been obtained. Although not all decays in the ME spectrum could be measured, it was also shown that inclusion of the decays of the remaining states does not much alter the composition of the ME's, nor the decay of the zero order states.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. Majewski for many stimulating discussions and for his contributions in the preliminary experiments and to Professor D. W. Pratt for critical reading of the manuscript. We thank Mr. D. Bebelaar (University of Amsterdam) for technical advice and Dr. W. Ubachs (University of Nijmegen) for his assistance during the experiments. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO).

[1] B. J. van der Meer, H. T. Jonkman, J. Kommandeur, W. L. Meerts, and W. A. Majewski, Chem. Phys. Lett. **92**, 565 (1982).
[2] B. J. van der Meer, Harry T. Jonkman, and Jan Kommandeur, Laser Chem. **2**, 77 (1983).
[3] A. Amirav and J. Jortner, J. Chem. Phys. **84**, 1500 (1986).
[4] P. J. de Lange, B. J. van der Meer, K. E. Drabe, J. Kommandeur, W. L. Meerts, and W. A. Majewski (submitted).
[5] H. T. Jonkman, K. E. Drabe, and J. Kommandeur, Chem. Phys. Lett. **116**, 357 (1985).
[6] P. J. de Lange, K. E. Drabe, and J. Kommandeur, J. Chem. Phys. **84**, 538 (1986).
[7] W. Majewski and W. L. Meerts, J. Mol. Spectrosc. **104**, 271 (1984).
[8] K. E. Drabe, J. Langelaar, D. Bebelaar, and J. D. W. Voorst, Chem. Phys. **97**, 411 (1985).
[9] W. Majewski, Opt. Commun. **45**, 201 (1983).
[10] W. D. Lawrance and A. E. W. Knight, J. Phys. Chem. **89**, 917 (1985).
[11] W. J. Schutten (private communication, 1985).
[12] K. Nakamura, J. Am. Chem. Soc. **93**, 3138 (1971).
[13] K. K. Innes, J. P. Byrne, and I. G. Ross, J. Mol. Spectrosc. **12**, 125 (1967).